SHINING APS LIGHT ON NANOSCALE OXIDATION

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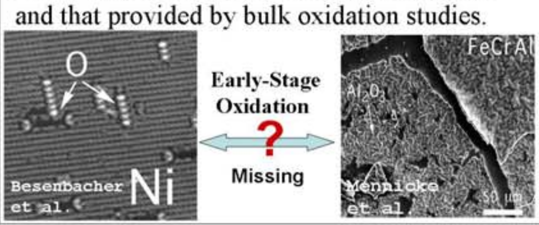
Introduction

Despite the enormous economic importance of metal oxidation, our knowledge of the underlying mechanistic processes is extremely limited. In particular, a substantial gap exists between the information available from surface-science studies, *i.e.*, at low oxygen coverage, and that provided by bulk oxidation studies.



Abstract

Using our environmental chamber at BESSRC Sector 12-ID, we are able to study the overall kinetics from oxygen surface absorption to nucleation, growth, and coalescence of oxide islands, and the phase and strain development in the oxide during oxidation. By measuring the stability of oxide islands as a function of oxygen partial pressure (pO_2) at different temperatures, the phase boundary between oxide growth and reduction was determined.

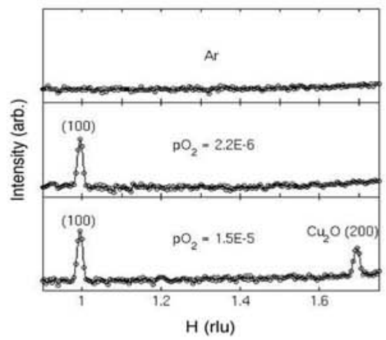
Scientific Objective

- To bridge the gap between surface science and bulk oxide studies.
- To control the structure, morphology, size and distribution of oxide islands; to pattern oxide nanostructures on surfaces by controlling nano oxidation.
- To produce modified metal surfaces with unique properties by controlled oxidation — Apply the new understanding to practical problems such as passivation, catalysis, etc.

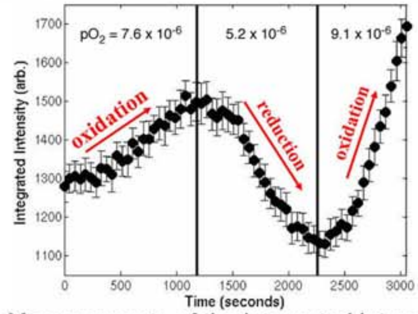
Experimental approach

In-situ oxidation chamber(BESSRC Sector 12)

- Highly precise control system of oxygen partial pressure.
- Highly accurate measurement of strain and phase development.
- Global reaction rate in the early-stage oxidation.

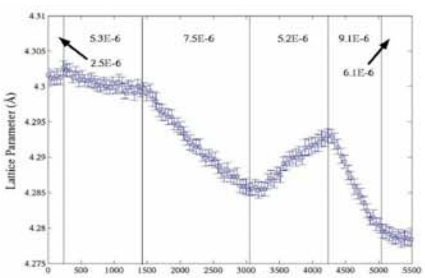


In-plane (H00) scans at 475°C of the sample in varying pO_2. After exposure of the initially clean surface to $pO_2 = 2.2 \times 10^{-6}$ Torr, a peak appears at (100) due to the formation of an ordered c(2 x 2) surface structure. Raising the pO_2 to 1.5×10^{-5} Torr results in oxidation to form Cu2O nano-islands that co-exist with the c(2 x 2) structure.

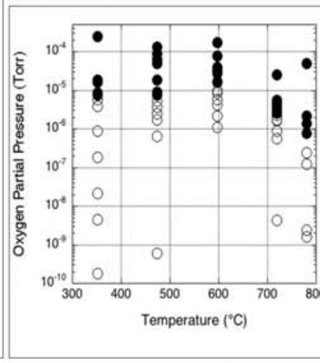


Measurements of the integrated intensity of the Cu2O (200) Bragg reflection in varying pO2 revealed that small changes in pO2 could result in a change from oxidation to reduction (or vice versa). The temperature during the measurements shown was 475°C.

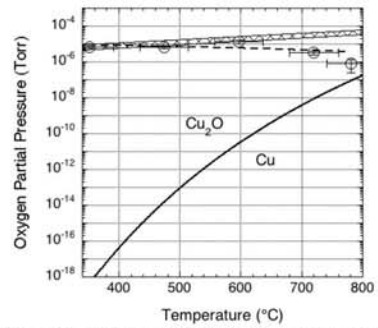
Oxidation of Cu(100) at 450 ° C and different oxygen pressures



Oxide nano-islands exhibit large reversible changes in lattice parameter, up to 0.5%, in response to changes in oxygen partial pressure. Such behavior is consistent with nano-islands having a much larger stoichiometric range than the bulk oxide.



The pO_2 where behavior switches from oxidation (filled) to reduction (open), determines the Cu-Cu_2O phase boundary.



The pO_2 for equilibrium between Cu_2O nano-islands and the Cu surface was determined to be several orders of magnitude larger than the bulk phase boundary; the temperature dependence was also much weaker.

Major Accomplishments

- Nanosize oxide islands show much higher dissociation oxygen partial pressure than the bulk material.
- The pO_2 for equilibrium between Cu_2O nano-islands and the Cu surface exhibit much less temperature dependence.
- Cu_2O lattice parameter depends strongly on the oxygen pressure.

Future plans

- Investigate the early-stage oxidation of Cu(110) and Cu(111).
- Examine the early-stage oxidation of Cu-Ni and Cu-Pd alloys.
- Study hydrogen storage and catalysis, which also involve vapor/solid reactions.

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